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Citation for the original published paper (version of record):

Vieceli, N., Casasola, R., Lombardo, G. et al (2021). Hydrometallurgical recycling of EV lithium-ion batteries: Effects of incineration on the
leaching efficiency of metals using sulfuric acid. Waste Management, 125: 192-203.
http://dx.doi.org/10.1016/j.wasman.2021.02.039

Waste Management 125 (2021) 192–203

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Hydrometallurgical recycling of EV lithium-ion batteries: Effects of incineration on the leaching efficiency of metals using sulfuric acid

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ARTICLE INFO

Article history:
Received 20 August 2020
Revised 19 February 2021
Accepted 20 February 2021

Keywords:
Lithium-ion batteries
Recycling
Incineration
Hydrometallurgy
Carbothermic reduction
Waste valorization

ABSTRACT

The growing demand for lithium-ion batteries will result in an increasing flow of spent batteries, which must be recycled to prevent environmental and health problems, while helping to mitigate the raw materials dependence and risks of shortage and promoting a circular economy. Combining pyrometallurgical and hydrometallurgical recycling approaches has been the focus of recent studies, since it can bring many advantages. In this work, the effects of incineration on the leaching efficiency of metals from EV LIBs were evaluated. The thermal process was applied as a pre-treatment for the electrode material, aiming for carbothermic reduction of the valuable metals by the graphite contained in the waste. Leaching efficiencies above 70% were obtained for Li, Mn, Ni and Co after 60 min of leaching even when using 0.5 M sulfuric acid, which can be linked to the formation of more easily leachable compounds during the incineration process. When the incineration temperature was increased (600–700 °C), the intensity of graphite signals decreased and other oxides were identified, possibly due to the increase in oxidative conditions. Higher leaching efficiencies of Mn, Ni, Co, and Li were reached at lower temperatures of incineration (400–500 °C) and at higher leaching times, which could be related to the partial carbothermic reduction of the metals.

1. Introduction

In 1991, Sony Corporation commercialized the first lithium-ion battery (Ozawa, 1994), employing a lithium cobalt oxide ($LiCoO_2$) and a non-graphitic carbon (lithiated coke LiC_6) as cathode and anode, to power small portable devices (Julien et al., 2016). Since then, the Li-ion technology has grown significantly and has replaced other relatively low-voltage battery technologies, such as Ni-Cd and Ni-MH, in many applications (Lu et al., 2018).

Nowadays, LIBs (lithium-ion batteries) are the technology of choice to power portable electronic devices and are also the most promising option to power electric vehicles (EV) and energy storage systems, due to characteristics including small volume, lightweight, high battery voltage, high energy density, long charging-discharging cycle, large temperature range and no memory effect (Scrosati et al., 2011; Zhang et al., 2013; Nishi, 2001; Kim et al., 2012).

The growing demand in the LIB market will consequently result in an increasing spent battery waste flow, which must be recycled (Dorella and Mansur, 2007, Yang et al., 2016). Some materials contained in LIBs are potentially toxic, including metals such as copper, nickel and lead, and organic chemicals, such as toxic and flammable electrolytes containing $LiClO_4$, $LiBF_4$, and $LiPF_6$ (Meshram et al., 2014). Furthermore, some of the LIBs materials are considered critical due to their increasing economic importance and their risk of shortage, since they are concentrated in a few countries and their supply can face geopolitical risks.

Spent LIBs are also an important secondary source of some metals, which are found in these batteries at very high concentrations, sometimes even higher than in their natural ores (Dorella and Mansur, 2007). If spent LIBs are disposed of properly, these metals can be recovered and reused, alleviating the pressure on natural resources. Moreover, these wastes pose a threat to the environment and human health (Zhang et al., 2013). Thus, recycling spent LIBs helps to mitigate environmental problems and reduces the gap between demand and supply of metals, contributing to conserve natural resources (Yang et al., 2016; Zhu et al., 2012).

Recycling of LIBs can include pre-treatment stages for discharging and dismantling, followed by mechanical treatments that take advantage of different physical properties of the components to separate and enrich them, for example by sieving, and magnetic

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https://doi.org/10.1016/j.wasman.2021.02.039
0956-053X/

and air separation (Zhao et al., 2019). Then, the recycling flow generally follows a hydrometallurgical or a pyrometallurgical approach. A detailed review of processes currently employed for recycling LIBs from mobility appliances was recently published by Mossali et al. (2020).

Hydrometallurgy is considered a more suitable technology than pyrometallurgy from an environmental and health point of view. It allows a higher recovery of elements with a purity grade, lower energy consumption, and no air emissions (Li et al., 2015). On the other hand, thermal pre-treatment helps to separate battery components, simplifies the discharging process, and it can also be used to remove carbon and organic compounds, and to decompose PVDF binder, but it requires treatment of gases (Vezzini, 2014; Hanisch et al., 2015).

Nowadays, the benefits of combining pyrometallurgical and hydrometallurgical processes have driven progress and research in the field of recycling (Lombardo, 2019), which has been the topic of many recent studies. Liu et al. (2019) classify these methods as mild recycling methods, which are normally pyrometallurgical-dominant and combine with hydrometallurgical methods. Such combined processes aim to reduce the consumption of energy and reagents, increasing efficiencies with promising application perspectives. Some recent studies that take advantage of combining both types of processes are presented in Table 1. Studies where a hydrometallurgical approach was not tested, but where the benefits of a pyrometallurgical approach can result in better results in the hydrometallurgical route, were also included.

Sun and Qiu (2011) used vacuum pyrolysis to improve the separation of the active cathode material from aluminum foils. The best results were obtained at 600 °C. The effect of pyrolysis on the composition of the battery cell materials as a function of treatment time and temperature was investigated by Lombardo et al. (2019). A reducing thermal treatment followed by acid leaching was studied by Yang et al. (2016) to recover Al and Cu foils and transition metals from LIBs. By this process, the current collectors were completely separated from the active materials. Zhang et al. (2020a) also investigated the use of pyrolysis of $LiCoO_2$ to remove the organic binder, and at the same time reduce Co^{3+}, improving its leaching efficiency.

Currently, vacuum pyrolysis is considered an alternative pre-treatment and compared with traditional processes prevents release of toxic gases to the environment at lower temperatures more than under atmospheric pressure (Sun and Qiu, 2011). Vacuum pyrolysis is also combined with carbothermic reduction to enhance lithium recycling efficiency (Liu et al., 2019). To date, many authors have been investigating the potential of carbothermic reduction as a pre-treatment of LIBs as it can be seen in Table 1.

Li et al. (2016) studied this process using graphite from the anode, where roasting was followed by a wet magnetic separation to remove elements converted to the metal form. Hu et al. (2017) studied reducing roasting, adding lignite as a carbon source to convert the valuable metals into more easily leachable forms, while Liu et al. (2018) used additional coke with a similar goal. Zhang et al. (2020b) investigated the thermal reduction treatment of spent NMC (nickel manganese cobalt oxide) cathode materials, employing the anodic graphite as a reductant. The valuable metals were then leached without reducing agents.

The special heating properties of microwaves were also recently applied for the carbothermic reduction of spent LIBs, which was investigated by Fu et al. (2020) and Zhao et al. (2020).

Considering that recent studies have mainly used pyrolysis as a method to promote a carbothermic reduction of cathode material, in this work incineration was used as an alternative process. In this context, the main goal of this study was to investigate the effect of using incineration in an oxygen atmosphere on the leaching efficiency of LIBs with sulfuric acid, without adding any other reducing agent. The incineration was performed as a thermal pre-treatment to promote the carbothermic reduction of the electrode material, and its effect on the leaching efficiency was tested. Hence, the proposed thermal pre-treatment could prevent the use of reducers in the leaching processes, such as hydrogen peroxide, which is normally used.

Thus, in this study the cathode material of spent LIBs was incinerated at different temperatures along with the anode containing graphite, aiming for carbothermic reduction of the valuable metals, which is expected to convert them into more easily leachable forms. The effects of incineration on the leaching efficiency were evaluated by leaching the incinerated samples at different temperatures with sulfuric acid. Leaching tests using reagent grade oxides and metals were also performed for comparison purposes.

2. Materials and methods

2.1. Battery dismantling and sampling

Lithium-ion batteries (NMC chemistry) were kindly provided by Volvo Car Corporation without charge. They were manually dismantled, their plastic cover was removed, the electrolyte was evaporated in a fume hood and the electrode layers were separated. The average weight of each pouch cell was 553.1 g ± 0.2 g and comprised 19 layers of anode and 18 layers of cathode. Each cell was approximately 22.5 cm long and 16.4 cm wide.

A circular pressing puncher (2 mm of diameter) was used to obtain representative samples from the electrode layers, using the same number of layers of cathodes and anodes, without any further pre-treatment. The samples were then ground using a universal mill crusher (IKA M20) and were subjected to thermal treatment by incineration and to leaching tests.

2.2. Thermal treatment by incineration

Samples weighing 6 g were inserted in a quartz tube (700 mm long and 30 mm diameter). To perform the thermal treatments, a tubular furnace (Nabertherm GmbH Universal Tube Furnace RT 50-250/13) was used. A constant flow of 340 mL/min of air was pumped through the tube to ensure the combustion of the samples, which were heated at 400, 500, 600 and 700 °C for 90 min. These temperatures were selected based on the range of temperatures reported in the literature, also considering that the removal of PVDF is expected to start from 400 °C.

2.3. Leaching tests using sulfuric acid

Leaching tests were performed in a 150 mL titration vessel with a thermostat jacket. The reactor was covered with a lid to collect samples and to insert an overhead mechanical stirrer. The stirring speed was set at around 300 rpm. The leaching temperature was set at 50 °C to observe the effects of different temperatures of incineration on the leaching efficiency. The leaching temperature was controlled using a thermal bath connected to the vessel. No additional reducer was used in the tests to evaluate the effect of the carbothermic reduction on the leaching efficiency of the samples.

Acid solutions were prepared using sulfuric acid (95%) and Milli-Q water. The acid concentration was the same for all tests (2 M H_2SO_4), except when experiments changing the concentration of acid were performed. The liquid to solid ratio (L/S) was set at 50 mL to 1 g of sample (50:1), to reduce the effect of sampling. A sample weight of 2 g was used in each test, which was obtained using the quartering method.

Table 1
Results of published studies using a thermal pre-treatment with potential to improve the leaching efficiency (conditions corresponding to the best combinations). n.a.: not applied.

Reference	Process	Materials	Thermal treatment temperature (°C)	Thermal treatment time (min)	Leaching reagents	Leaching temperature (°C)	Leaching time (min)	L/S ratio	Max Li%	Max Co%	Max Mn%	Max Ni%
Sun and Qiu (2011)	Vacuum pyrolysis	Cathode electrodes (mobile LIBs), $LiCoO_2$ without anode	600	30	H_2SO_4 (4% vol) + H_2O_2 (1% vol)	40	60	30	97	100	–	–
Li et al. (2016)	Roasting + wet magnetic separation	$LiCoO_2$ + graphite	<1000	30	n.a.	–	–	–	>98	>95	–	–
Yang et al. (2016)	Reducing roasting + acid leaching	Cathode and anode assemblies	600	15	H_2SO_4 (4 M) + H_2O_2 (2 × theoretical amount)	90	120	8	–	99	85	98.5
Hu et al. (2017)	Reducing roasting with lignite + leaching	Cathode material + lignite	650	180	H_2SO_4 (3.5 M)	85	180	5	>84	>99	>99	>99
Liu et al. (2018)	Reducing roasting + leaching	NMC 111 + 10% coke	650	30	H_2SO_4 (2 M)	25	120	10	>93	>98	>98	>93
Demarco et al. (2019)	Thermal treatment	LIBs fine powder (from mobiles)	700	120	DL-malic (2 M) + H_2O_2 (6% vol)	95	60	20	>93	>90	>99	–
Pindar and Dhawan (2019)	Reduction in atmospheric conditions + leaching	Mixed cathode active material (from mobiles) + recovered graphite	900	45	Analytical procedure (4 M H_2SO_4)	90	30	10	>90	~86	~90	–
Wang et al. (2019)	Reducing roasting with Al + leaching	Cathode powders ($LiCoO_2$)	600	60	Alkaline leaching + acid leaching (H_2SO_4)	50	30	20	>93	>99	–	–
Liu et al. (2019)	Reducing roasting + leaching	NMC (mix) + carbon black	550	30	H_2SO_4 (4 M)	90	30	10	>93	>99	>99	>99
Fu et al. (2020)	Microwave carbothermic reduction	NMC 111 + graphite	900 (500 W)	30	HCl (1 M)	50	20	~66	>94	>91	>90	>92
Yue et al. (2018)	Reducing roasting + acid leaching + solvent extraction	Cathode material ($LiCoO_2$) + graphite from anode	600	120	H_2SO_4 (2.25 M)	80	30	10	~100	~100	–	–
Zhang et al. (2020b)	Reducing roasting with graphite + leaching	Mixed electrode materials + graphite	600	180	H_2SO_4 (1.05 times of the theoretical amount)	85	60	6	>99	>99	>97	>99

Samples were taken at different time intervals (indicated in the section of results) and were filtered with a syringe–filter to stop the reaction. The solution obtained after the filtration was diluted in 0.5 M nitric acid and analyzed by ICP-OES (iCAP™ 6000 Series) to determine the concentration of the metals leached during the tests. Untreated and incinerated samples were characterized by X-ray powder diffraction (XRPD, Siemens D5000 diffractometer), under the following conditions: Cu K_α radiation, 10–80° 2θ range, 15 rpm rotation speed, generator settings of 40 mA and 40 kV. Analytical interpretation was performed using EVA software and the JCPDS database.

Some tests were performed using Ni, Co and Mn in their metallic form (Manganese powder, 99.99% trace metal basis, Sigma Aldrich; Nickel powder, <50 μm, 99.7% trace metal basis, Sigma Aldrich; Cobalt powder, <150 μm, ≥99.9% trace metal basis, Sigma Aldrich) and in the oxide form normally used to synthesize LIBs (Nickel(II) oxide, powder 97%; Acros Organics; Manganese(IV) oxide; Reagent Plus®, ≥99%, Sigma Aldrich; Cobalt(II,III) oxide, powder < 10 μm; Sigma Aldrich). In this case, the chemicals used were of reagent grade and tests were performed to compare with the results of the leaching tests of LIBs and to better understand the leaching behavior of these metals.

3. Results and discussion

The initial composition of the untreated samples (initial samples which were not incinerated) and of the samples incinerated at different temperatures are presented in Table 2. A general trend of increase in the content of different metals was observed, which was proportional to the increase in the temperature of incineration. This is compatible with the loss of weight verified by Lombardo et al. (2020), who also studied the same samples. The loss of weight for samples incinerated for 90 min was around 16% at 400 °C, 23% at 500 °C, 28% at 600 °C and around 33% at 700 °C.

The composition of the initial sample is richer in Mn and, when the content of each metal in the cathode material is related to its respective molar mass, the untreated sample is compatible with the cathode composition $LiNi_{1/4}Mn_{1/2}Co_{1/4}O_2$ (NMC 121). This composition is not normally reported in the literature as a commercial cathode material for EV LIBs, which can indicate that the samples used in the tests comprised a mixture of different cathode materials.

3.1. Effect of molar acid concentration on leaching efficiency

Preliminary tests varying the molar concentration of sulfuric acid in the leaching tests (from 0 to 2.5 M) were performed. The range of concentrations tested is comparable with other studies reported in the literature (Table 1). The expected increase in the leaching efficiency with increase in acid concentration could limit the access of the effects of incineration on the efficiency. Therefore, concentrations of sulfuric acid above 2.5 M were not tested. The samples used in these tests were thermally pre-treated by incineration at 500 °C for 90 min. Samples were taken after 10, 30 and 60 min of leaching. Leaching was performed at 50 °C. The results are presented in Fig. 1, where the leaching efficiency of each metal is represented as recovery (%) on the y-axis.

It is possible to observe that the dissolution of metals tends to increase when increasing the leaching time and higher extractions were obtained after 60 min of leaching, except for copper. The leaching efficiency also increased with the molar concentration of acid. However, the extraction was very high even when low acid concentrations were used, which could be related to the thermal pre-treatment of the samples.

Lithium exhibited a slightly different behavior. Dissolution of lithium was high even after 10 min of leaching, and showed small improvement when the leaching time was increased. Additionally, lithium was the only metal extracted when no acid was used - about 30% Li was leached using just water, regardless of the leaching time. This could be related to an inefficient decomposition of $LiPF_6$, which was suggested by Lombardo et al. (2020), based on the concentration of P in samples incinerated under the same conditions. According to Marinos and Mishra (2016), during water leaching, lithium from the electrolyte ($LiPF_6$) gets into the solution. In the process they proposed, the material was shredded and submitted to magnetic separation. The remaining material was then leached at room temperature for 1 h using water to solubilize $LiPF_6$, and the lithium concentration varied from about 30 to 200 mg/L. The lithium concentration obtained in this study when water was used as a solvent was about 200 mg/L. Furthermore, it is important to highlight that other lithium compounds resulting from the carbothermic reaction, such as Li_2CO_3, also have some solubility in water – 13 g/L H_2O at 25 °C, according to Haynes et al. (2016).

Mn, Ni and Co exhibited similar behavior and their leaching efficiencies increased with acid concentration and leaching time. Leaching efficiencies of about 70% were obtained for these metals after 60 min, even at an acid concentration of 0.5 M, which can be considered low when compared to the literature (Table 1). The extraction of Al remained lower than other metals, but in general also increased with leaching time and acid concentration. Al is considered an impurity in the purification of the solutions and high concentrations are generally avoided.

In this work, no further pre-treatment of the electrodes was applied and the Al and Cu were not removed to evaluate their behavior in the incineration and subsequent leaching. However, from an industrial perspective, the Al and Cu content can be lower when these metals are removed by physical pre-treatment. Additionally, the removal of Al and Cu can be improved by thermal pre-treatment, which according to Hanisch et al. (2015) reduces the adhesion between coating and foil, which can be removed by physical treatment. Yang et al. (2016) also observed a very clean separation of the active cathode materials from Al foil after heating at high temperatures in high purity nitrogen, which could allow the foil to be directly recycled.

Table 2
Elemental composition of the untreated sample and of the samples incinerated at different temperatures.

Thermal Treatment	Content (%)					
	Li	Mn	Ni	Co	Al	Cu
Untreated	2.4 ± 0.1	10.2 ± 0.2	4.8 ± 0.1	5.1 ± 0.1	9.5 ± 0.6	15.1 ± 3.7
400 °C	3.0 ± 0.1	13.0 ± 0.6	5.8 ± 0.3	5.8 ± 0.3	7.1 ± 0.5	16.6 ± 1.5
500 °C	3.3 ± 0.1	13.8 ± 0.2	6.6 ± 0.1	7.1 ± 0.2	8.9 ± 0.1	16.0 ± 0.5
600 °C	3.4 ± 0.3	15.0 ± 1.1	6.6 ± 0.5	6.7 ± 0.5	8.3 ± 0.4	16.8 ± 0.2
700 °C	3.5 ± 0.1	15.6 ± 0.4	7.0 ± 0.2	7.0 ± 0.2	7.9 ± 0.7	17.4 ± 0.4
LOD (mg/L)	0.019	0.003	0.009	0.010	0.049	0.015

*LOD: limit of detection.

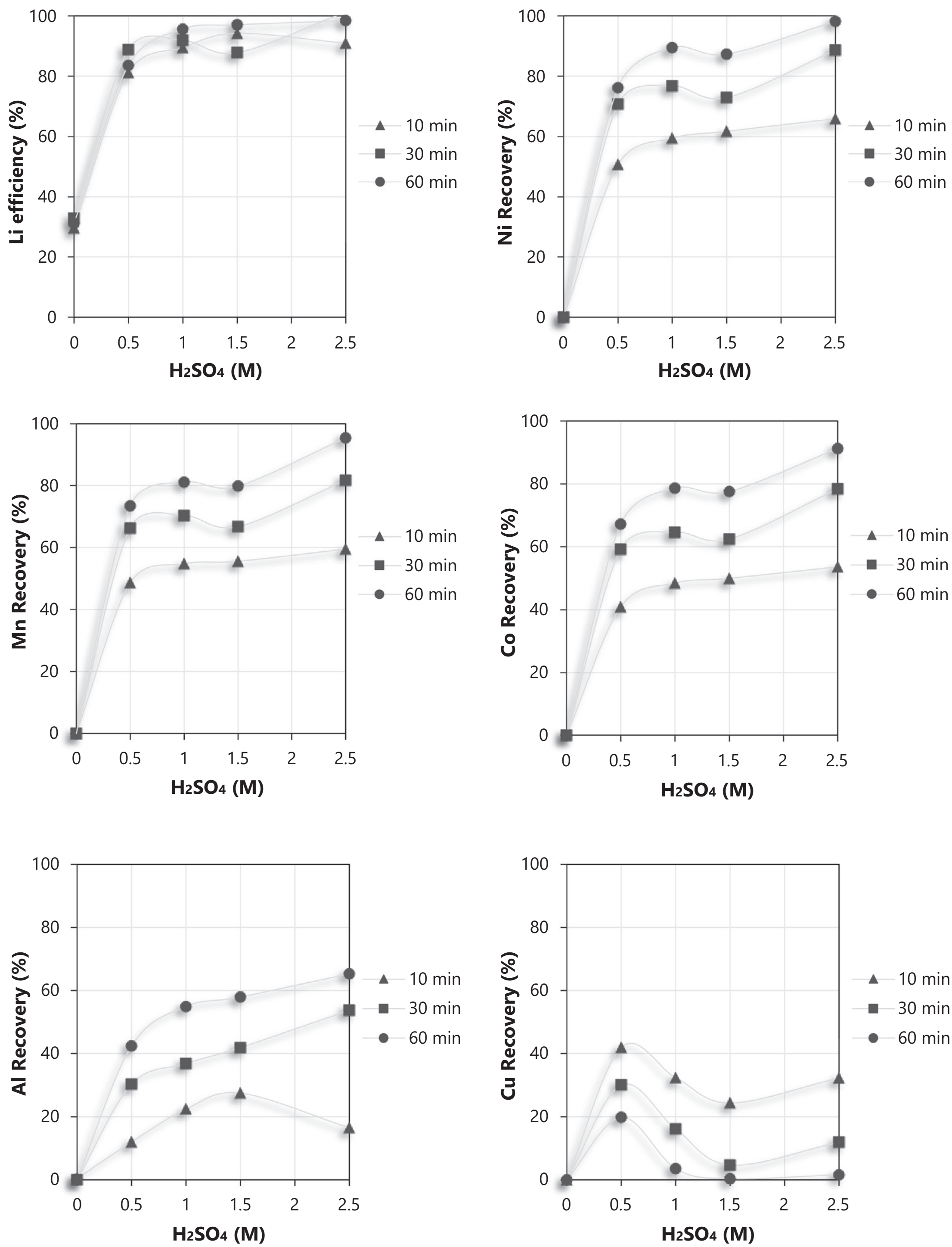

Fig. 1. Leaching efficiency of metals at different molar concentrations of H_2SO_4 and different leaching times. Leaching conditions – L/S: 50 and leaching temperature: 50 °C. Incineration conditions – 500 °C for 90 min.

The leaching of Cu exhibited a different behavior, since its dissolution increased with 0.5 M of sulfuric acid and then decreased, which might be related to changes in the oxidative state from Cu^0 to Cu^{2+} and again to Cu^0. A similar behavior was observed by Vieceli et al. (2018) during the leaching of LIBs with sulfuric acid and sodium metabisulphite as a reducer.

In this study, leaching tests were performed using only sulfuric acid, but considering the high dissolution of metals from incinerated samples even at mild acid conditions, additional tests using more environmentally friendly acids could be carried out in future investigations. The next experiments were performed using 2 M of H_2SO_4, to avoid constraining the leachability and to try to obtain the highest leaching efficiency of metals from samples incinerated at different temperatures.

3.2. Compositional changes

Compositional changes of the incinerated samples at different temperatures were evaluated by XRPD and were compared with an untreated sample (not incinerated). The results are shown in

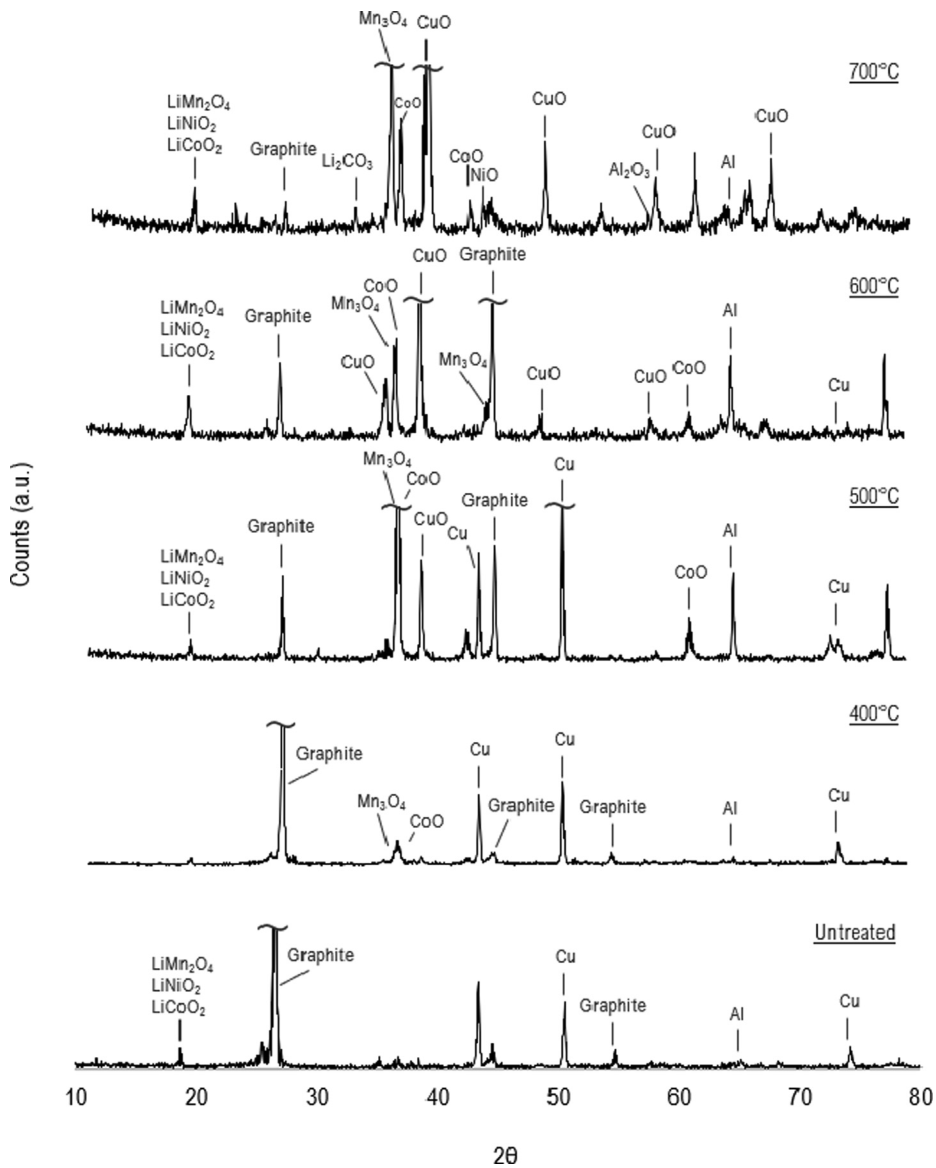

Fig. 2. X-ray diffractogram of the untreated sample and of samples treated by incineration at different temperatures.

Fig. 2. It is possible to observe that the intensity of the signals of graphite decreased with the increase in the temperature, which is compatible with the lower carbon content observed in the samples treated at 600 and 700 °C by Lombardo et al. (2020). At 700 °C, signals of CuO, Al_2O_3 and other oxides were also identified, indicating an increase in the oxidizing conditions that could be responsible for decreasing the leaching efficiency of metals. Furthermore, the presence of lithium oxides (18°) was identified in all samples, indicating that the carbothermic reduction was not completely achieved. This was more pronounced with the increase in temperature and can be related to the predominance of oxidizing conditions and the decrease in the carbon content.

3.3. Effect of carbon content on leaching efficiency

Lombardo et al. (2020) studied the effects of incineration in an oxidative atmosphere on the composition of spent LIBs and their dependence on treatment time and temperature. In that study, the carbon present in the batteries was found to trigger a carbothermic reduction of the metal oxides. However, when the temperature increases, the oxidative conditions promote the removal of graphite, and at 700 °C the carbothermic reduction is restrained. Demarco et al. (2019) employed a thermal pre-treatment of the $LiCoO_2$ from spent batteries of mobile telephones as a procedure to remove PVDF and carbon and they also observed the absence of graphite after 2 h of treatment at 700 °C, indicating that it was combusted, although carbothermic reduction was not intended in that work. Zhang et al. (2020b) also observed a positive relation between the leaching efficiency and the graphite dosage in samples thermally treated in an argon atmosphere. The same positive relation between graphite dosage and better reduction of the cathode material was verified by Pindar and Dhawan (2019).

Therefore, considering the important role of graphite in the carbothermic reduction of metals from the electrodes, the molar ratio between metals and carbon was evaluated. The molar mass of the metals present in the incinerated samples at different temperatures was related to the carbon content (Fig. 3). The carbon content of samples treated under the same conditions used in this study was previously evaluated by Lombardo et al. (2020) and the initial materials used in both studies were also the same. For this reason, the carbon content reported by Lombardo et al. (2020) was used to estimate the molar ratio between the metals and carbon, considering a manganese-rich composition NMC 121 (carbon content for samples thermal treated for 90 min according to Lombardo et al.

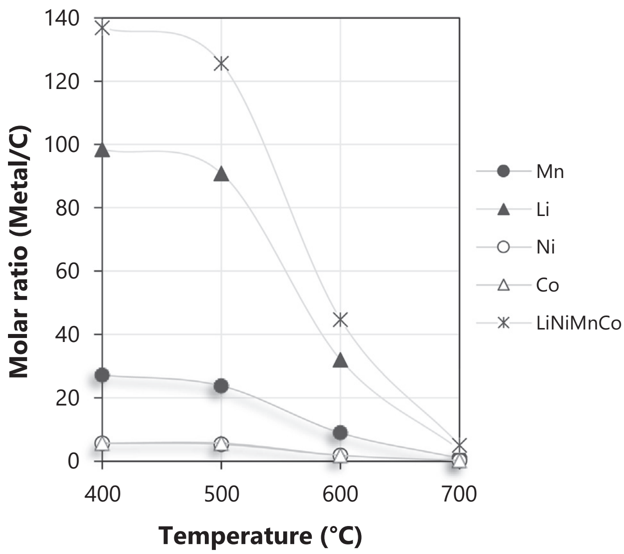

Fig. 3. Molar ratio between the metals of the electrodes and the carbon content (the carbon contained in the samples was estimated based on the results of Lombardo et al. (2020), who used the same initial samples and the same incineration conditions).

(2020) – 400 °C: 19.1%, 500 °C: 15.7%, 600 °C: 5.5%; 700 °C: 0.6%). The carbon content in the untreated samples (not incinerated) was 41% (±3). It is important to highlight that although Lombardo et al. (2020) tested the same samples and incineration conditions as this study, their work focused only on the thermodynamic aspects related to the incineration and no leaching tests were performed by them. Thus, considering that a hydrometallurgical process will be needed after the thermal pre-treatment, the effects of incineration on the leaching efficiency were studied in the present work.

It is possible to observe that the increase in the temperature of incineration is accompanied by a decrease in the molar ratio between the metals to be reduced (Mn, Li, Co and Ni). This could be related to the high decrease in the carbon content at higher temperatures (only 0.6% at 700 °C), which is mainly responsible for inducing the carbothermic reduction and the decrease of which could lead to an increase in the oxidizing conditions. Thus, the low carbon content in the samples treated at high temperatures (600 and 700 °C) could be a limiting factor for carbothermic reduction and could be the reason why lower leaching efficiencies were obtained for samples treated at these conditions, as is discussed in the next section.

According to Hanisch et al. (2015), under an oxygen atmosphere, the decomposition of PVDF begins at 350 °C and at 550 °C almost all binder mass is volatized. At 580 °C, mass loss of carbon black begins, followed by graphite loss at 650 °C. The battery active material $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ does not volatize in this range of temperatures. Zhao et al. (2020) studied the microwave-assisted reduction roasting of the cathode material from LIBs using anthracite as a carbon source, which also promoted a carbothermal reduction reaction. By XRD the authors observed that the mixed powder started to decompose and led to the formation of metal oxides CoO, NiO and MnO. They also observed that the argon gas introduced into the furnace continuously carried away the CO gas not completely reacted and, for this reason, it could be necessary to provide additional carbon.

3.4. Effect of thermal treatment temperature on leaching efficiency

The leaching efficiency of the samples pre-treated by incineration is shown in Fig. 4. The leaching efficiency of lithium was similar for samples treated at 400, 500 and 600 °C, while lower results were seen at 700 °C. The leaching of lithium was very fast and achieved about 85% after 1 min for samples incinerated from 400 to 600 °C. The leaching efficiency of Li was also very high for untreated samples and reached 86% after 5 min of leaching, indicating that Li is present in forms that are easily leached under the acid conditions used (2 M H_2SO_4).

Regarding the leaching efficiency of Mn, Ni and Co, it is possible to observe that incineration at 400 °C led to higher leaching efficiencies of these metals, which also increased with the leaching time (~78% Mn, ~90% Ni and ~85% Co after 60 min of leaching). On the other hand, incineration at 700 °C led to the lowest results for Mn, Ni and Co (~30% Mn, ~41% Ni and ~24% Co after 60 min of leaching), indicating that incineration at this temperature could promote the formation of compounds that are not easily leached under the tested conditions. Moreover, as was previously discussed, the lower carbon content at higher temperatures can constrain the carbothermic reduction, making the leaching efficiency lower. Intermediate results were obtained for samples incinerated at 500 °C.

Lombardo et al. (2020) used HSC software to study the thermodynamic considerations of incineration of the same material used in this work. The samples were thermally treated under different temperatures and times (including those applied in the current work). According to the authors, CO_2 is the most favored product at temperatures below 700 °C and the calculations indicate that the main products include Mn_3O_4, Ni_3O_4, Co_3O_4 and Li_2CO_3 (Eq. (1)).

$$12Li(Ni_{1/4}Mn_{1/2}Co_{1/4})O_2 + 7C + 6O_2 \rightarrow Co_3O_4 + 2Mn_3O_4 + Ni_3O_4 + 6Li_2CO_3 + CO_2 \quad (1)$$

According to Lombardo et al. (2020), a combination of high temperatures and oxygen will induce the combustion of the graphite present in the LIBs, and CO_2 would be the most thermodynamically favored product of this reaction at temperatures lower than 700 °C, according to Eq. (2).

$$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)} \quad (2)$$

Lombardo et al. (2020) also indicated that as the reaction proceeds, Co_3O_4 can be further reduced to CoO and Co. Ni_3O_4 can be reduced to NiO and Ni, while Mn_3O_4 can be also reduced to MnO_2 and MnO, but the reduction to the metallic form of Mn was not foreseen by their model.

However, when the residual content of carbon was evaluated, a huge decrease was observed in the samples incinerated at 600 °C and 700 °C (as discussed in Section 3.3). Thus, it can be concluded that when the carbon content decreases, it becomes a limiting factor for the carbothermic reduction. Thus, it is possible that with the increase in the incineration temperature and the consequent decrease in the carbon content, oxidizing conditions will prevail and the formation of Co_3O_4, Ni_3O_4 and Mn_3O_4 will be favored, which can explain the diminished leaching efficiency at higher temperatures.

Yang et al. (2016) studied a process based on reducing thermal treatment before acid leaching in a high purity nitrogen atmosphere. The authors observed the decomposition of PVDF at 500 °C and the formation of CO_2 from 500 to 650 °C, which the authors related to redox reactions between the cathode conductor acetylene black and the active cathode materials, where the transition metals in the active cathode material are reduced from a high charge to a low charge state, making their leaching easier and more efficient.

According to Zhang et al. (2020b), the production process of $LiNi_xCo_yMn_zO_2$ materials occurs at high temperatures in an oxidizing atmosphere. Therefore, the chemical bonds M—O are very strong and the valence state of the transition metals is high. Thus,

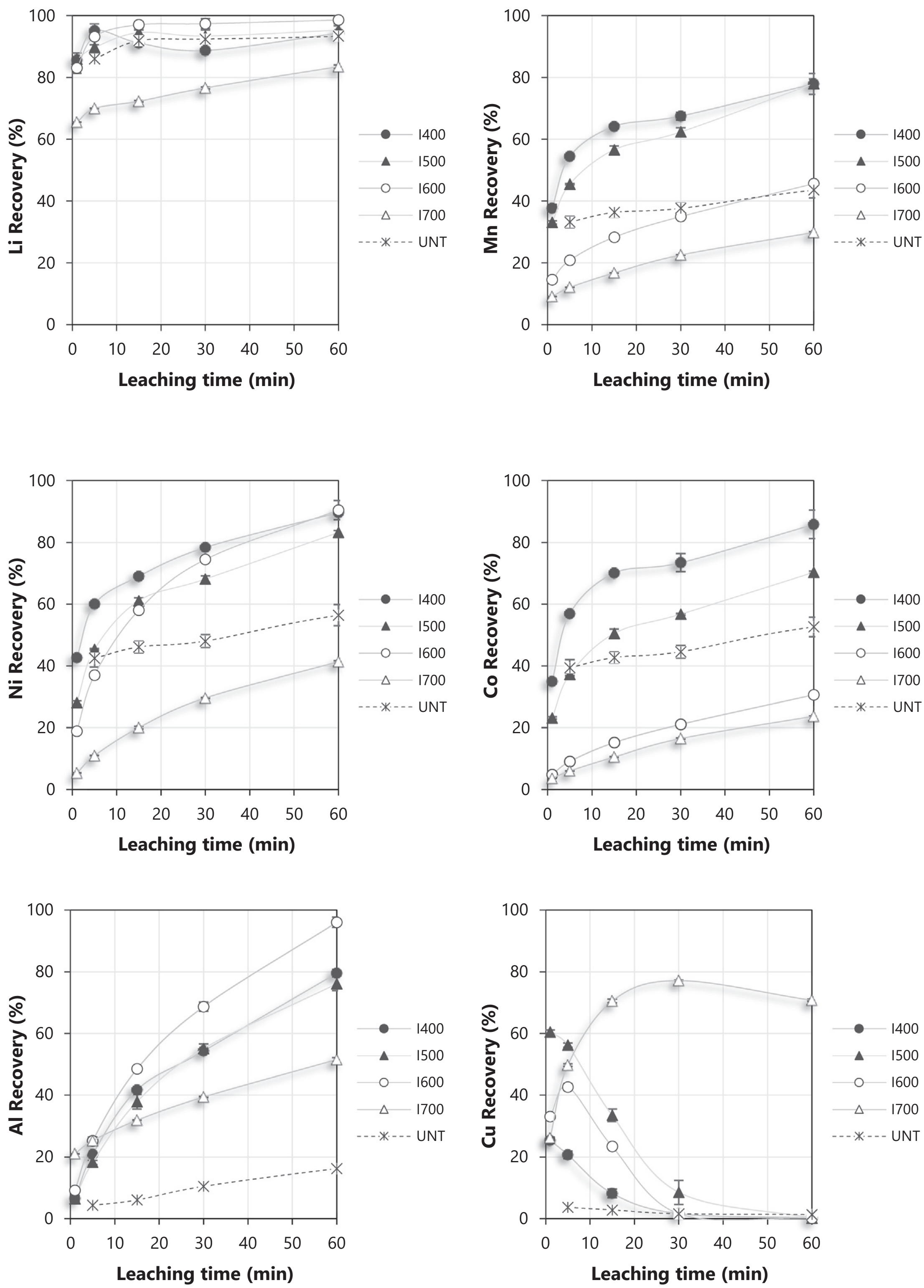

Fig. 4. Leaching efficiency of different metals from samples thermally pre-treated by incineration at different temperatures, according to the leaching time. Leaching conditions – L/S: 50:1, 2 M H_2SO_4 and leaching temperature: 50 °C. Legend: UNT – untreated sample. Standard deviation is based on triplicates.

the principle to recover these same metals includes reducing their valence state, breaking M—O bonds and destroying material structures (Gao et al., 2018; Zhang et al., 2020b).

Concerning the leaching efficiency of Al, this also increased with leaching time and samples incinerated at 600 °C had higher leaching efficiencies (96% after 60 min of leaching), while increasing the incineration temperature led to diminished Al leaching efficiency, with the worst results at 700 °C (16% after 60 min of leaching). The decrease in the leaching efficiency of Al at 700 °C can be related to the formation of Al_2O_3 (Eq. (3)) due to the increase in the oxidative conditions of the airflow, which was also identified by more pronounced signals in the XRD diffractograms (Fig. 2) and which has a very low solubility even in strong acids.

$$Al + O_{2(g)} \rightarrow Al_2O_3 \quad (3)$$

Sun and Qiu (2011) also observed that when heating the cathode active material under atmospheric pressure at 600 °C, the cathode electrode became breakable, indicating that the electrode easily oxidizes at high temperatures. Shin et al. (2005) observed a negative effect on the leaching efficiency of cobalt after incineration at 900 °C, which was attributed to the surface of lithium cobalt oxide being covered with molten aluminum, hindering the leaching process. Despite the melting point of Al being in the range of temperature tested in this study (660 °C), no sign of melting was observed, possibly due to the formation of Al_2O_3, as reported by Lombardo et al. (2020).

In contrast, copper exhibited the opposite behavior and its highest leaching efficiency was obtained at 700 °C, while the lowest leaching efficiency was verified at 400 °C (~1% after 60 min). The leaching efficiency of Cu also increased with leaching time for the samples incinerated at 700 °C and reached the highest result after 30 min of leaching (almost 80%). For samples treated at 400, 500 and 600 °C, the leaching efficiency of Cu increased at the beginning of the tests (1 to 5 min) and then decreased to almost 0% after 1 h.

Lombardo et al. (2020) studied the thermodynamic behavior of samples thermally treated under the same oxidative conditions used in this work. Using XRPD analysis, the authors also observed that the graphite signals almost disappeared at 700 °C and the residual carbon content was also very low (<1%), indicating that organic compounds were almost completely consumed. Additionally, the resulting airflow would cause strong oxidation of the Cu foils and CuO (Eq. (4)) signals became more evident in the diffractograms, which could explain the higher leaching efficiency of Cu at 700 °C.

$$Cu + O_{2(g)} \rightarrow CuO \quad (4)$$

Thus, the leaching behavior of copper could be explained by differences in its oxidative state. As can be observed in the XRD spectra, signals corresponding to CuO are more pronounced in the samples treated at 600 and 700 °C (Fig. 2). On the other hand, at 400 °C, signals corresponding to the more reduced metallic form of copper can be identified.

Based on the results, it is possible to conclude that under the tested conditions, incineration using lower temperatures (400–500 °C) promoted better leaching efficiencies, which could be related to the carbothermic reduction of the metals caused by CO and CO_2 produced during the reaction of carbon (from anodic graphite) with the oxygen present in the airflow. A partial carbothermic reduction of the cathodic material prevents the formation of metallic forms, which during the leaching step using sulfuric acid would react releasing H_2. This is undesirable and would need additional requirements related to gas treatment. Yang et al. (2019) tested an oxidizing roasting at around 500 °C to recover graphite from LIBs, however, only the anode was tested. Therefore, the possibility of recovering the remaining graphite from the samples used in this study could be considered in further studies.

Additional tests were performed to evaluate the leaching behavior of Co, Ni and Mn oxides and metals, individually, to better understand the results obtained in the previous tests based on the individual leaching efficiency of these metals and oxides (Fig. 5). Reagent grade chemicals were used in these tests and the samples were not incinerated.

The dissolution of cobalt from its metallic form increased with temperature and leaching time. For the metallic form, the dissolution of cobalt at 60 °C and 80 °C was faster and exceeded 90% at 15 min and 30 min, respectively. At 120 min of leaching, the results for 40 °C, 60 °C and 80 °C were similar and exceeded 90%.

The dissolution of cobalt from cobalt oxide (Co_3O_4) was very low under the tested conditions and was less than 1% for all tests. For this reason, different units were used on the y-axis to represent the dissolution. Despite the low dissolution of cobalt from Co_3O_4, increase in the temperature and time promoted a slight increase in the dissolution. These results are in accordance with Haynes et al. (2016), who stated that metallic cobalt is soluble in diluted acid while cobalt oxides are soluble in strong acids. According to Hubli et al. (1997), Co_3O_4 is more stable than CoO and more difficult to solubilize, being dissolved with a reducing agent to convert Co^{+3} to Co^{+2}.

Vu et al. (1980) also studied the leaching of metallic cobalt and oxides and they observed that the dissolution of cobalt oxides in sulfuric acid was significantly lower than the dissolution of metallic cobalt. According to them, the dissolution of metallic Co, CoO and Co_3O_4 is very different due to their chemical structures and is dependent on the oxidation state (Co > CoO > Co_3O_4), which is also compatible with the high dissolution of metallic cobalt and the very low dissolution of Co_3O_4 observed experimentally (Fig. 5).

The dissolution mechanism of metallic cobalt in a leachate in the presence of oxygen is believed to be that an oxygen atom or molecule is adsorbed on the cobalt metal surface, acting as an electron receiver. At these conditions, the bonding between oxygen and cobalt is very weak and breaking it occurs easily during the leaching, causing the metal to rapidly dissolve. On the other hand, the bonding between oxygen and cobalt in the cobalt oxides is chemical and very strong. Therefore, breaking these bonds requires significantly more energy and as a result, the dissolution rate of the oxides is lower than the metal. Moreover, in the spinel structure of Co_3O_4, this bonding is extremely strong and its dissolution is even slower (Vu et al., 1980). Therefore, the lower leaching efficiencies of cobalt at higher temperatures could be related to the increase in the oxidative conditions. This will result in the formation of Co_3O_4, which is more difficult to leach (Eq. (5))

$$3CoO + 1/2O_{2(g)} \rightarrow Co_3O_4 \quad (5)$$

According to Bhuntumkomol et al. (1982), cobalt oxides and nickel oxides have a distinct leaching behavior and cobalt oxides have a lower dissolution rate, which could be used to selectively separate both oxides. The results of the dissolution of nickel from nickel oxide (NiO) and from its metallic form are shown in Fig. 5, where it is possible to compare the dissolution of both forms. The dissolution of Ni from the metallic form increased with the leaching temperature and time. The dissolution reached 96% after 60 min of leaching at 80 °C, while at 60 °C, the dissolution was 85% after the same time of leaching. At 25 °C and 40 °C, the dissolution was always less than 50%.

The dissolution of nickel oxide (NiO) was faster and reached 95% and 100% at 60 °C and 80 °C respectively, after only 15 min of leaching. Under the tested conditions, the dissolution of Ni from NiO was faster and led to higher results when compared to the metallic form, although both cases had a high leaching efficiency when compared to Mn and Co.

Considering that both nickel forms (metallic and oxides) exhibited a high leaching efficiency under the tested conditions, it could explain the higher leaching efficiency of nickel for the samples thermally treated, when compared to Mn and Co, even for samples incinerated at 600 °C.

According to Haynes et al. (2016), both nickel metal and oxide are soluble in strong acids. According to Bhuntumkomol et al. (1982) and Nut (1970), metallic nickel is reasonably soluble in acid provided that oxygen is present. Nickel oxides, in contrast

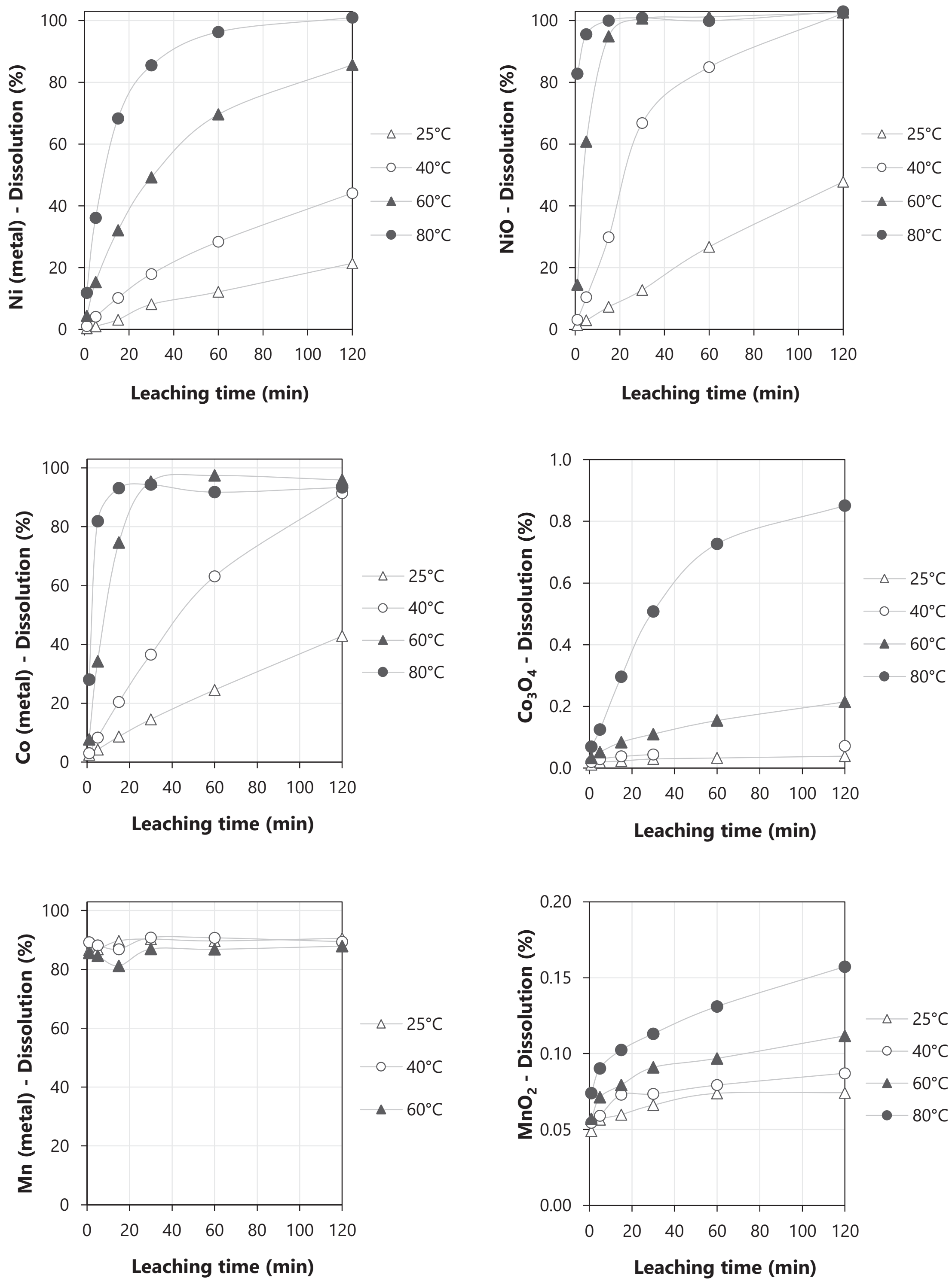

Fig. 5. Leaching of metals (left side) and oxides (right side) at different temperatures and leaching times. Leaching conditions – L/S: 50:1 and 2 M H_2SO_4 All materials were of reagent grade. Tested oxides: MnO_2, Co_3O_4, NiO.

to cobalt, do not seem to form stable oxides with a valence above two under ambient conditions and NiO is believed to be reasonably soluble in mineral acids. Pichugina et al. (2002) also verified that the dissolution of nickel oxides increases with increased temperature. The authors observed that the dissolution of nickel oxide is accelerated by oxidizers, while it is slowed by reducers. This can explain the higher dissolution obtained for oxides (Ni^{2+} > Ni^0).

Nut (1970) also investigated the role of certain ions in the nickel oxide dissolution. It was verified that the presence of reducing ions seems to decrease the dissolution of nickel, and the stronger the reducing ability of the ion is, the larger the effect in decreasing the dissolution rate of NiO. According to Nut (1970), the effect of cations in decreasing the dissolution rate of NiO increases in the order of Mn^{2+} < Hg^{2+} < Fe^{2+}. This effect could also play a role in the dissolution of nickel from oxides present in LIBs.

Manganese in the metal form was readily dissolved in acid after just 1 min of leaching for all tested temperatures, which was expected considering that manganese in the metallic form readily dissolves even in diluted acids (Haynes et al., 2016; National Pollutant Inventory, 2018). For this reason, tests at 80 °C were not performed, given the fast reaction observed at lower temperatures accompanied by gas release (H_2). On the other hand, the dissolution of MnO_2 is very low, less than 1% for all conditions, and was represented using a different scale. These differences could be related to the lower leaching efficiency of Mn from incinerated samples when compared to Ni and Co, since the formation of Mn in the metallic form during the incineration was not expected, as previously discussed.

Zhang et al., 2020b studied the carbothermic reduction of NMC cathode material from spent LIBs using graphite from the anode. At 600 °C, the authors observed metallic phases of Ni and Co, which was considered undesirable by them since it requires more energy to achieve higher temperatures. Moreover, they considered that leaching oxides would be easier than the metallic form, which would generate the flammable and dangerous gas H_2 (Eqs. (6) to (8)) during the acid leaching. According to the same authors, by effectively obtaining low valent metal oxides, an easier leaching process could be attained, involving lower energy consumption, with no H_2 emissions and more facile conditions for a complete leaching.

$$Ni + H_2SO_4 \rightarrow H_{2(g)} + NiSO_4 \tag{6}$$

$$Co + H_2SO_4 \rightarrow H_{2(g)} + CoSO_4 \tag{7}$$

$$Mn + H_2SO_4 \rightarrow H_{2(g)} + MnSO_4 \tag{8}$$

Therefore, it is possible to conclude that under the tested conditions, a partial carbothermic reduction of the samples using lower temperatures of incineration (400 to 500 °C) had a positive effect, increasing the leaching efficiency of metals from LIBs.

It is worth noting that other factors could also affect the dissolution of metals from LIBs pre-treated by incineration, for example, the leaching temperature, the stirring speed and the L/S ratio, and should be studied in further investigations where the results obtained in this work could be a support. It is also important to highlight that given the potential of releasing flammable and toxic gases during the incineration process, these methods should be associated with efficient and stringent gas treatment.

4. Conclusions

Incineration was tested as a thermal pre-treatment of the electrode material of LIBs, which can promote a carbothermic reduction of the metals, affecting their leaching efficiency – leaching efficiencies above 70% for Li, Mn, Ni and Co, were achieved even when using low concentrations of sulfuric acid (0.5 M). When the temperature of incineration was increased to 600 and 700 °C, the intensity of the graphite signals decreased and other oxides were identified. This was compatible with the decrease in the leaching efficiency of Li, Mn, Ni, and Co, from samples incinerated at higher temperatures, and could be related to the complete combustion of the carbon sources. The decrease in the reductive conditions would increase the oxygen flow in the furnace, hindering the carbothermic reduction and promoting the formation of compounds that are more difficult to leach. Thus, the results demonstrate that a partial carbothermic reduction of the electrode material would be more advantageous. Under the tested conditions, lower incineration temperatures (400–500 °C) seem to favor the formation of CO and CO_2, which reacts with the electrode material starting a carbothermic reduction and helps to improve the leaching efficiency of metals from LIBs without additional reducers that are usually needed.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This research was supported by the Swedish Energy Agency – Battery fund (Grant No: 40506-1 and 48204-1). The authors would like to acknowledge the support of Volvo Car Corporation for providing the samples and valuable discussion. R. Casasola expresses her gratitude to the European Cooperation in Science and Technology, COST, for the Short Term Scientific Mission (STSM ID 115396), funded by COST Action grant number CA18224, Green Chemical Engineering Network towards upscaling sustainable processes.

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